

AD A 050508

AD No.

DDC FILE COPY

12
SC

FINAL REPORT
ENVIRONMENTALLY IMPROVED AFFF
N00173-76-C-0295

BY
THE ANSUL COMPANY
MARINETTE, WISCONSIN 54143

DECEMBER 13, 1977

DDC
RECEIVED
FEB 28 1978
RECEIVED

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

(9) FINAL REPORT.
(6) ENVIRONMENTALLY IMPROVED AFFF.
(15) N00173-76-C-0295 new

BY
THE ANSUL COMPANY ✓
MARINETTE, WISCONSIN 54143

(11) 13 Dec 77 (12) 45 p.

DECEMBER 13, 1977

ADDITIONAL FOR	
NTIS	Write Section <input checked="" type="checkbox"/>
DGC	Diff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
<i>letter on file</i>	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. and BY SPECIAL
A	

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

403 478

Gu

TABLE OF CONTENTS

	PAGE
1.0 INTRODUCTION	1
1.1 CONTRACTOR'S PROPOSAL	1
1.1.1 PROPOSAL OBJECTIVE	1
1.1.2 PROGRAM STEPS	2
1.2 CONTRACT WORK STATEMENT	3
1.2.1 INTRODUCTION	3
1.2.2 TECHNICAL TASKS	4
1.3 PERFORMANCE FIRE MEASUREMENTS	6
2.0 EXPERIMENTAL TECHNIQUES	7
2.1 BIOLOGICAL OXYGEN DEMAND	7
2.1.1 APPARATUS	7
2.1.2 REAGENTS	8
2.1.3 PROCEDURE	11
2.1.4 BOD CALCULATION	14
2.2 CHEMICAL OXYGEN DEMAND	15
2.2.1 APPARATUS	15
2.2.2 REAGENTS	15
2.2.3 PROCEDURE	16
2.2.4 CALCULATIONS	18
2.3 AQUATIC TOXICITY	18
2.4 PHYSIOCHEMICAL PROPERTIES AND PERFORMANCE . .	18
3.0 EXPERIMENTAL RESULTS	20
3.1 ALTERNATE METHODS FOR THE DETERMINATION OF AFFF SOLUTION CONCENTRATION	27
3.2 SUGGESTED SOLUTION	28
3.3 THE WATER SOLUBLE DYE APPROACH	29
3.4 RECOMMENDED PROCEDURE	30
3.5 EXPERIMENTAL	36

TABLE OF CONTENTS (CONTINUED)

	PAGE
4.0 CONCLUSIONS	38
BIBLIOGRAPHY	

LIST OF TABLES

		PAGE
I	BOD RESULTS OF EXPERIMENTAL COMPOUNDS EXPRESSED AS MGMS O ₂ /MGM COMPOUNDS	21
II	COD RESULTS OF EXPERIMENTAL COMPOUNDS	22
III	96-HOUR AQUATIC TOXICITY INVESTIGATION ON FUNDULUS HETEROCLITUS (MUMMICHOGS).	24
IV	96-HOUR AQUATIC TOXICITY INVESTIGATION ON FUNDULUS HETEROCLITUS (MUMMICHOGS)	25
V	28 SQ.FT. FIRE PERFORMANCE OF EXPERIMENTAL AFFF FORMULATIONS	26

LIST OF FIGURES

		PAGE
1	PERCENT TRANSMISSION VS. PROPORTIONING: EXPERIMENTAL LOW SOLVENT AFFF K76'-312 CONTAINING 120 PPM DYE . . .	31
2	PERCENT TRANSMISSION VS. PROPORTIONING: 3M LIGHT WATER AFFF CONTAINING 120 PPM DYE	32
3	AFFF CONCENTRATE CONTAINING 120 PPM DYE AND SELECTED SEA WATER DILUTIONS	33
4	PERCENT TRANSMISSION VS. PROPORTIONING: EXPERIMENTAL LOW SOLVENT AFFF K76'-312-102 CONTAINING 40 PPM DYE .	34
5	AFFF CONCENTRATE CONTAINING 40 PPM DYE AND SELECTED SEA WATER DILUTIONS	35

1.0

INTRODUCTION

This investigation was undertaken to try to gain some insights into how the chemical composition of aqueous film-forming foam (AFFF) concentrates effects the environmental properties of these fire extinguishing agents. Since this is a relatively new area of concern and interest, there will be differences of opinion in how to approach the investigation. The contractor's original proposal and the final work statement are presented below for purposes of clarity in outlining the work and criteria used in this investigation.

1.1

Contractor's Proposal

1.1.1

Proposal Objective

- (a) The purpose of this work is to explore the development of experimental AFFF formulations that would exhibit reduced impact on the environment while retaining certain fire suppression characteristics. In particular, it is proposed to examine the effect of the AFFF formulation components on the biological oxygen demand of the concentrate. In light of results previously obtained with available concentrates, fish toxicity is not considered to be a problem and therefore will not be investigated.

- (b) It is furthermore proposed that the requirements of MIL-F-24385, Amendment 8, and the proposed revision thereto, will not apply to the present investigation. There will in all probability be a trade-off between biological impact and physiochemical characteristics. Fire performance and corrosion characteristics are of primary importance, whereas refractive index, pH, viscosity, foam expansion ratio, and surface interfacial tension are of lesser importance.
- (c) The generally accepted method for determining proportioned or premixed solution composition is to measure the refractive index of the solution. In order to get acceptable accuracy and precision with field type refractometers, solvent levels of 15-20% are currently used in commercial products. It is assumed that these levels are deleterious from a biological aspect. Some effort will be expended in evaluating alternate analytical techniques for the measurement of AFFF solution concentration.

1.1.2

Program Steps

- (a) Raw Material BOD₂₀ - Twenty-day BOD studies will be conducted on typical fluorocarbon surfactants, hydro-

carbon surfactants and solvents. The purpose will be to determine the effect of chemical composition on BOD₂₀.

- (b) BOD₂₀ Design Experiment - Investigate the effect of component concentration and type on BOD₂₀. Candidate formulations will be selected based on this investigation.
- (c) Formulation Design Experiment - Formulations will be selected based on the BOD₂₀ investigation and screened for fire performance and physiochemical properties. This will include corrosion characteristics and concentrate stability, in addition to fire performance.
- (d) Analytical Methods Evaluation - An investigation of alternate analytical methods for determining solution concentration will be conducted to determine if a simple method for use in the field is feasible.

1.2 Contract Work Statement

1.2.1 Introduction

The present formulations with respect to fire suppression are highly effective. However, improvements are desired in the

environmental area, i.e., development of compositions that have a reduced impact on the environment without loss of fire suppression effectiveness.

1.2.2

Technical Tasks

- (a) The Contractor shall explore the development of experimental AFFF formulations that would exhibit a reduced impact on the environment while retaining fire effectiveness.
- (b) The proposed study will examine the effect of AFFF formulation components on the biological oxygen demand (BOD), chemical oxygen demand (COD), biodegradability, toxicity toward sewage bacteria, fish toxicity, effect of component concentration on selected environmental/biological parameters, formulation design experiments, and analytical methods evaluation.

1.2.2.1

Task I - Raw Material BOD₂₀ and COD

Twenty-day BOD studies shall be conducted on typical fluorocarbon surfactants, hydrocarbon surfactants and solvents. The purpose will be to determine the effect of chemical composition on BOD₂₀. Chemical oxygen demand (COD) measurements,

toxicity toward sewage bacteria, and fish toxicity (kill fish) will also be made on the above materials.

1.2.2.2 Task II - Biodegradability and BOD₂₀ Design Experiment

Investigate the effect of component concentration on biodegradability and BOD₂₀. Candidate formulations will be selected based on this investigation.

1.2.2.3 Task III - Formulation Design Experiment

Formulations shall be selected based on the BOD₂₀ biodegradability investigation and screened for fire performance and physiochemical properties. This will include corrosion characteristics and concentrate stability, in addition to fire performance.

In the event that a more highly concentrated material (to be used in less than a 6% solution) is desired, all environmental properties shall be adjusted to a 6% datum base.

1.2.2.4 Task IV - Analytical Methods Evaluation

An investigation of alternate analytical methods for determining solution concentration shall be conducted to determine if a simple method for use in the field is feasible.

1.3

Performance Fire Measurements

Compare fire performance of the new formulation with that of formulation currently manufactured and employed in the field, by the same test methods. Fire performance test procedures shall conform to Paragraph 4.7 of MIL-F-24385 (NAVY), Amendment 8, as applicable.

2.0

EXPERIMENTAL TECHNIQUES

Previous work^(1, 2, 3) conducted in the area of environmental characteristics of AFFF was directed at determining the following with regard to commercially available AFFF liquid concentrates:

- BOD (Biological Oxygen Demand)
- COD (Chemical Oxygen Demand)
- Acute Toxicity (Concentration required to produce a certain level of mortality in a particular species after exposure for a certain time.)

2.1

Biological Oxygen Demand

The BOD determinations were conducted in accordance with the procedures given in the literature⁽⁴⁾. The detailed procedure is given as follows:

2.1.1

Apparatus

- (a) Model 54 YSI dissolved oxygen monitor with Model 5720 YSI self-stirring BOD bottle probe and Model 5735 cable adaptor. (All of these are available from Fisher Scientific.)
- (b) Incubation BOD bottles (300 ml) with ground-glass stoppers (acid-washed before use).

- (c) Incubator thermostatically controlled at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

All light must be excluded from the incubator to prevent formation of DO by algae in the sample.

2.1.2

Reagents

- (a) Distilled water of the highest quality containing less than 0.01 mg/l copper and free of chlorine, chloramines, caustic alkalinity, organic material, or acids.
- (b) Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate (KH_2PO_4), 21.75 g dipotassium hydrogen phosphate (K_2HPO_4), 33.4 g disodium hydrogen phosphate heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$), and 1.7 g ammonium chloride (NH_4Cl) in about 500 ml distilled H_2O and dilute to 1 liter. The pH of this buffer solution should be 7.2 without further adjustment.
- (c) Magnesium sulfate solution: Dissolve 22.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
- (d) Calcium chloride solution: Dissolve 27.5 g anhydrous CaCl_2 in distilled water and dilute to 1 liter.
- (e) Ferric chloride solution: Dissolve 0.25 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.

- (f) Acid and alkali solutions 1N: For neutralization of samples which are either caustic or acidic.
- (g) Sodium sulfate solution 0.025N: Dissolve 1.575 g anhydrous Na_2SO_3 in 1000 ml distilled water. This solution is not stable and should be prepared when needed.
- (h) Seeding material: May be collected from receiving water 2-5 miles below discharge point of industrial waste water.
- (i) Manganese sulfate solution: Dissolve 480 g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, 400 g $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, or 364 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in distilled water, filter and dilute to 1 liter.
- (j) Alkali-iodide-azide reagent: Dissolve 500 g sodium hydroxide, NaOH (or 700 g potassium hydroxide, KOH), and 135 g sodium iodide, NaI (or 150 g potassium iodide, KI), in distilled water and dilute to 1 liter. To this solution add 10 g sodium azide, NaN_3 , dissolved in 40 ml distilled water. Potassium and sodium salts may be used interchangeably.

- (k) Sulfuric Acid, Concentrate: The strength of this acid is about 36 N; therefore, 1 ml acid is equivalent to about 3 ml of the alkali-iodide-azide reagent.
- (l) Starch solution: Prepare an emulsion of 5-6 g potato, arrowroot, or soluble starch in a mortar or beaker with a small quantity of distilled water, allow to boil a few minutes, and let settle overnight. Use the clear, supernatant liquid. This solution may be preserved with 1.25 g salicylic acid per liter or by the addition of a few drops of toluene.
- (m) Sodium thiosulfate stock solution 0.10N: Dissolve 24.82 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in boiled and cooled distilled water and dilute to 1 liter. Preserve by adding 5 ml chloroform or 1 g NaOH per liter.
- (n) Standard sodium thiosulfate titrant, 0.025N: Prepare either by diluting 250.0 ml sodium thiosulfate stock solution to 1000 ml or by dissolving 6.205 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in freshly boiled and cooled distilled water and diluting to 1000 ml. Standard sodium thiosulfate solution may be preserved by adding 5 ml chloroform or 0.4 g NaOH per liter. Standard sodium thiosulfate solution, exactly 0.0250N, is equivalent to 0.200 mg DO per 1.00 ml.

Standardize with dichromate, dilute exactly 100.0 ml of 0.250N potassium dichromate solution used in the COD determination to 1000 ml.

Standardization of sodium thiosulfate solution 0.0250N: Dissolve approximately 2 g KI, free from iodate, in an Erlenmeyer flask with 100 to 150 ml distilled water; add 10 ml 1 + 9 H_2SO_4 , followed by exactly 20.00 ml standard dichromate (0.0250N) solution. Place in dark for 5 minutes. Dilute to 400 ml and titrate the liberated iodine with the thiosulfate titrant, adding starch toward the end of the titration when a pale straw-color is reached. Exactly 20.00 ml of 0.0250N thiosulfate should be required when the solutions under comparison are of equal strength.

- (o) Special reagent - potassium fluoride solution: Dissolve 40 g $\text{KF} \cdot 2\text{H}_2\text{O}$ in distilled water and dilute to 1000 ml.

2.1.3 Procedure

The dilution water to be used should be distilled water of the highest purity and as near 20°C as possible. The water should also be saturated with DO^* . Place the desired amount of distilled water in a suitable bottle and add 1 ml each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride

solutions for each liter of dilution water.

For this test procedure, 25 ml of seed water (1/3 municipal sewage treatment plant water and 2/3 river water) was added for each liter of dilution water.

The samples should be neutralized to pH 7.0 with either the 1N H_2SO_4 or NaOH.

For this test, 5, 10 and 20 ml of the pre-diluted samples were pipetted into the 300 ml BOD bottles which were then topped off with the seeded dilution water and placed in the incubator. Also placed in the incubator was a bottle of the seeded, aerated dilution water. Care must be taken when filling the bottles with the seeded dilution water to ensure that no air bubbles are entrained. The bottles will be stored in the incubator for 20 days at $20^\circ\text{C} \pm 1^\circ\text{C}$. The DO of the samples and the seeded dilution water will be checked at 5, 10, 15 and 20 days.

Before checking the DO with the YSI DO meter, the meter will be calibrated using the DO value obtained by azide modification of the iodometric method for determining DO. Two BOD bottles will be filled with aerated distilled water. One will be titrated while the other will be used as a calibration standard.

The dissolved oxygen content of the samples and the seeded dilution water control were checked just prior to being placed in the incubator. They were found to be:

5 ml samples - 9.30 mg/l

10 ml samples - 9.20 mg/l

20 ml samples - 9.10 mg/l

Seed dilution water control - 9.30 mg/l

The procedure for the azide modification of the iodometric method for determination of DO follows:

- (a) To the sample as collected in the 300 ml bottle add 2 ml manganese sulfate solution followed by 2 ml alkali-iodide-azide reagent well below the surface of the liquid; stopper with care to exclude air bubbles and mix by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. When the settling has produced at least 100 ml clear supernate, carefully remove the stopper and immediately add 2 ml concentrated H_2SO_4 by allowing the acid to run down the neck of the bottle. Restopper and mix by gentle inversion until dissolution is complete. The iodine should be uniformly distributed

throughout the bottle before decanting the amount needed for titration. This amount should be 203 ml.

- (b) Titrate with 0.025N sodium thiosulfate solution to a pale straw-color. Add 1-2 ml (15 drops recommended) freshly prepared starch solution and continue the titration until the first appearance of blue color. Each ml of sodium thiosulfate required is equal to 1 mg/1 DO. The DO meter is then calibrated using this figure as a constant.

During the process of taking the DO readings, the DO probe must be rinsed and recalibrated before each measurement. The rinsing is necessary to prevent any carry-over between samples. After each measurement, the bottle is returned to the incubator as soon as possible.

2.1.4

BOD Calculation

The equation by which the BOD was calculated is as follows:

$$\text{mg/l BOD} = \frac{(D_1 - D_2) - B_1 - B_2}{P} f$$

D_1 = Original DO

D_2 = DO after incubation

B_1 = DO of dilution water before incubation

B_2 = DO of dilution water after incubation

f = Ratio of seed in sample to seed in control

P = Decimal fraction of sample used

f for 5 ml sample = .983

f for 10 ml sample = .967

f for 20 ml sample = .933

p =

5 ml sample at 1/5000 = 3.333×10^{-6}

1/12500 = 1.333×10^{-6}

1/8333 = 2.000×10^{-6}

10 ml sample at 1/5000 = 6.667×10^{-6}

1/12500 = 2.667×10^{-6}

1/8333 = 4.000×10^{-6}

20 ml sample at 1/5000 = 1.333×10^{-6}

1/12500 = 5.333×10^{-6}

1/8333 = 8.000×10^{-6}

2.2

Chemical Oxygen Demand

The COD determinations were conducted in accordance with the procedure given in the literature⁽⁴⁾. The detailed procedure is given as follows:

2.2.1

Apparatus

Reflux apparatus (250 ml Erlenmeyer or Florence flask with ground glass 24/40 neck and 300 mm Jacket Liebig, West, or equivalent condensers with 24/40 ground glass joint, heating mantle or hot plate.)

2.2.2

Reagents

(a) Standard potassium dichromate solution 0.250N

(12.259 g dried primary standard grade, 103°C for

two hours, in distilled water and dilute to 1000 ml.

Add .12 g sulfamic acid.)

- (b) Concentrated H_2SO_4 containing 22 g Ag_2SO_4 per 9-lb. bottle (1-2 days required for dissolution)
- (c) 0.10N standard $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$: Dissolve 39 g analytical grade $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled H_2O . Add 20 ml concentrated H_2SO_4 , cool and dilute to 1000 ml.
- (d) Ferroin indicator solution: Dissolve 1.485 g 1,10 phenanthroline monohydrate together with 0.695 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water (distilled) and dilute to 100 ml.
- (e) Silver sulfate, reagent powder (see b)
- (f) Mercuric sulfate, analytical grade crystals
- (g) Sulfamic acid, analytical grade (see a)

2.2.3

Procedure

- (a) Place 0.4 g HgSO_4 in the refluxing flask, add 20 ml of pre-diluted sample, swirl to mix. Add 10.0 ml 0.250N $\text{K}_2\text{Cr}_2\text{O}_7$. Carefully add 30.0 ml concentrated H_2SO_4

containing Ag_2SO_4 with mixing. Add 3 or 4 boiling chips (previously ignited at 600°C for 1 hour) or glass beads to prevent bumping.

- (b) Reflux for two hours, cool and wash down condensor neck with distilled water.
- (c) Dilute the mixture with distilled water to about 140 ml, cool to room temperature and titrate the excess dichromate with standard ferrous ammonium sulfate, using ferroin indicator. Generally 2-3 drops of indicator are used and the amount should not vary among samples. The color change is sharp, going from blue-green to reddish-brown.
- (d) A blank consisting of 20 ml distilled water instead of the sample, together with the reagents, is refluxed and titrated in the same manner.
- (e) Each day the ferrous ammonium sulfate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$) must be standardized. This is done by diluting 10.0 ml standard potassium dichromate solution to about 100 ml. Add 30 ml concentrated H_2SO_4 and allow to cool. Titrate with the ferrous ammonium sulfate titrant using 2-3 drops of ferroin indicator.

$$\text{Normality Fe (NH}_4)_2\text{(SO}_4)_2 = \frac{\text{ml K}_2\text{Cr}_2\text{O}_7 \times 0.25}{\text{ml Fe (NH}_4)_2\text{(SO}_4)_2}$$

2.2.4 Calculations

The equation used to calculate the COD follows:

$$\text{Mg/kg sample COD (straight compound)} = \frac{(a-b)c \times 8000}{\text{ml sample}} - \text{dilution ratio}$$

Where:

a = ml Fe (NH₄)₂(SO₄)₂ · 6H₂O used for blank

b = ml Fe (NH₄)₂(SO₄)₂ · 6H₂O used for sample

c = normality of Fe (NH₄)₂(SO₄)₂ · 6H₂O

sample size = 20 ml

To get COD of diluted sample, do not divide by dilution ratio.

2.3 Aquatic Toxicity

The aquatic toxicity investigation was conducted on the species fundulus heteroclitus (killi fish, mummichog) in accordance with NSRDC procedures⁽⁵⁾.

2.4 Physiochemical Properties and Performance

The determination of the physiochemical properties of the

experimental formulations and their fire performance characteristics were conducted in accordance with the procedures given in MIL-F-24385, Amendment 8.

3.0

EXPERIMENTAL RESULTS

The experimental aspects of this investigation were based upon the results obtained using 20-day BOD screening of various raw materials.

Aqueous film-forming foams can be broken down into three general components:

- Fluorochemical Surfactants
- Hydrocarbon Surfactants
- Solvents

Three compounds were selected as being typical for each one of these components. These compounds were selected and subjected to 20-day BOD studies. Based on these materials, the most likely combinations were formulated into AFFF concentrates and subjected to further screening.

- Fluorochemical Surfactants
 - Lodyne S-105 - anionic
 - Lodyne S-110 - amphoteric
 - Lodyne S-116 - cationic
- Hydrocarbon Surfactants
 - Deriphat D-160C - partial sodium salt of n-lauryl B - iminodipropionic acid

Tergitol 15-S-12 - nonionic surfactant based on linear alcohol functionality (isomer distribution C₁₁ - C₁₈)

Conco EL-30 - a sulfonic acid derivative of cocoa butter - anionic

Solvents (50/50 Mixtures)

Butoxy ethoxy propanol-2/hexylene glycol
Proposal B/ethylene glycol
Butyl carbitol/propylene glycol

The results of the BOD investigation are given in Table I.

Table I
BOD Results of Experimental Compounds
Expressed as mgms O₂/mgm Compounds

<u>Material</u>	BOD ₁₁	BOD ₁₅	BOD ₂₀
Lodyne S-105	.443	.409	.430
Lodyne S-110	.245	.272	.286
Lodyne S-116	.118	.059	.103
Deriphat D-160C	.336	.378	.431
Conco EL-30	.458	.423	.407
Tergitol 15-S-12	.150	.111	.121
BEP/HEG	.444	.440	.517
Propasol B/EG	1.070	.716	.957
BC/PG	1.109	.701	.899

The results of the COD determination are given in Table II and show little concentration dependence.

Table II
COD Results of Experimental Compounds

<u>Material</u>	<u>Dilution</u>	<u>COD (mgms/l)</u>
Lodyne S-105	1:12,500	776,875
Lodyne S-105	1:5,000	780,850
Lodyne S-110	1:12,500	498,000
Lodyne S-110	1:5,000	539,950
Lodyne S-116	1:12,500	368,500
Lodyne S-116	1:5,000	509,950
Deriphath D-160C	1:12,500	597,625
Deriphath D-160C	1:5,000	669,300
Conco EL-30	1:12,500	507,750
Conco EL-30	1:5,000	533,850
Tergitol 15-S-12	1:12,500	2,101,500
BEP/HG	1:8,333	2,064,917
Propasol B/EG	1:8,333	1,789,428
BC/PG	1:8,333	1,922,203

Based on these results, the most likely fluorochemical surfactant was Lodyne S-105. The hydrocarbon surfactants could either be Deriphath D-160C or Conco EL-30. Any of the solvent systems selected would be acceptable, assuming that a minimum BOD₂₀ to COD ratio of .15 can be used to define biodegradability.

Preliminary 28 sq.ft. fire testing eliminated Lodyne S-110 from further consideration due to poor extinguishment and burnback characteristics. The use of the solvent system Propasol B/Ethylene Glycol also resulted in poor expansion ratios (<2-3) and poor burnback resistance.

It was therefore decided to screen for fish toxicity based upon the following:

Lodyne S-105

Conco EL-30

Butyl Carbitol/Propylene Glycol

Butoxy Ethoxy Propanol-2/Hexylne Glycol

Previous work⁽⁶⁾ involving formulations using Deriphat D-160C as the hydrocarbon surfactant in experimental AFFF formulations had resulted in reasonably good fish toxicity values.

The results of the 96-hour aquatic toxicity studies on the fluorochemical (S-105) and the hydrocarbon surfactant (EL-30), as well as the two solvent systems, are given in Table III.

Table III
96-Hour Aquatic Toxicity Investigation
on Fundulus Heteroclitus (Mummichogs)

<u>Compound</u>	<u>Hour</u>	<u>LC₅₀ ppm</u>	<u>Confidence Limits</u>	<u>No Effect Level (ppm)</u>
			<u>95%</u>	
EL-30	48	46.0	34.6 - 61.2	--
	72	42.0	29.8 - 59.2	--
	96	34.5	23.8 - 50.0	15
S-105	48	3000	2521 - 3570	--
	72	2500	2136.8 - 2925.0	--
	96	2150	1869.6 - 2472.5	1300
50/50 Butyl	48	4800	4485.9 - 5136.0	--
Carbitol &	72	4350	4103.8 - 4611.0	--
Propylene Glycol	96	4125	4004.8 - 4248.8	3000
50/50 Hexylene	48	2150	1837.6 - 2515.5	--
Glycol & BEP	72	1875	1644.7 - 2137.5	--
	96	1690	1469.6 - 1943.5	1100

As a result of the 20-day BOD studies, the following formula-
tions were prepared and tested.

<u>Material</u>	<u>Formulation Number</u>			
	<u>F-117</u>	<u>F-118</u>	<u>F-121</u>	<u>F-122</u>
S-105	3.0%	3.0%	3.0%	3.0%
EL-30	4.0%	6.0%	--	--
D-160C	--	--	4.0%	6.0%
BC/PG*	5.0%	7.0%	5.0%	7.0%

*50%/50% mixture by weight of butyl carbitol and hexylene glycol.

The aquatic toxicity studies for these formulations is given in Table IV.

Table IV
96-Hour Aquatic Toxicity Investigation
on Fundulus Heteroclitus (Mummichogs)

Com- pound	Hour	LC ₅₀ ppm	Confidence Limits	No Effect Level (ppm)
			95%	
F-117	48	595	450.8 - 785.4	--
	72	455	388.9 - 532.4	--
	96	365	301.7 - 441.7	105
F-118	48	475	413.0 - 546.3	--
	72	435	381.6 - 495.9	--
	96	395	355.9 - 438.5	180
F-121	48	1855	1650.4 - 2070.2	--
	72	1385	1112.8 - 1565.6	--
	96	1315	1090.7 - 1497.9	1300
F-122	48	1850	1659.8 - 2090.2	--
	72	1365	1100.2 - 1580.4	--
	96	1330	1060.7 - 1508.8	1330

The 28 sq.ft. fire testing of these formulations is given in Table V. No appreciable changes in performance or foam quality were noted after aging at 150°F for 10 days.

Table V
28 Sq. Ft. Fire Performance of Experimental AFFF Formulations

Form. No.	Solution Conc.	90% Control Time (sec.)	Ext. Time (sec)	25% Burnback (sec.)	Exp. Ratio	25% Drain Time (sec.)
F-117	6F	18	24	480	6.6	204
F-117	6S	19	33	480	4.7	174
F-118	6F	18	24	480	7.6	260
F-118	6S	18	24	480	6.2	222
F-121	6F	19	23	480	6.8	230
F-121	6S	19	26	480	5.4	198
F-122	6F	18	24	480	6.7	207
F-122	6S	19	26	480	4.9	247

Based on the aquatic toxicity data contained in Table IV, the use of EL-30 as a hydrocarbon surfactant is deleterious from an environmental aspect even though the fire performance characteristics, as shown in Table V, are acceptable. It is also clear that higher solvent levels and higher hydrocarbon surfactant levels tend to give better foam quality. It should also be noted that these two components have little or no effect on the fire performance characteristics. It also substantiates the fact that the present use levels of 15-20% solvent have little or no effect on fire performance as well as foam quality, assuming a 5:1 expansion ratio is acceptable.

3.1

Alternate Methods for the Determination of AFFF Solution Concentration

In order to determine if analytical methods other than refractive index could be used to determine AFFF solution composition, the following study was undertaken. The ability to reduce the solvent levels would result in a product having a lower environmental impact and a lower cost to the end-user. To this end, the following investigation was undertaken.

Aboard Navy ships, aqueous film-forming foam (AFFF) is usually stored as a concentrate. When used to extinguish a fire, the concentrate is pumped through a proportioning device where it is mixed with sea water and this mixture is sprayed from a nozzle. Optimum AFFF performance requires that the proportioning be as close to 94 volumes of sea water to 6 volumes of AFFF concentrate as possible.

Because of possible mechanical shortcomings, the proportioning system may not achieve the optimum volume ratio and would require adjustment. Therefore, a means of determining the dilution of an AFFF concentrate is required. At present, refractive index is used to monitor the accuracy of

a proportioning system and to achieve a sufficiently large change in refractive index with dilution requires that a qualified AFFF concentrate contain 15 to 20% organic solvents. Since the surfactant active ingredient content of qualified AFFF concentrate is only in the range of 4-6%, the added solvent represents a 4-fold increase in the BOD loading of the system.

If an alternative method for monitoring the performance of a proportioning system can be developed, a significant decrease in the environmental impact of an AFFF system would be realized. This report describes the development of a simple field test method of measuring the dilution of AFFF concentrates.

3.2

Suggested Solution

Based on the results of investigation described below, the dilution of an AFFF concentrate can be accurately determined by the addition of a water soluble dye to the concentrate and measuring the absorbance of the proportioned solution with an inexpensive field colorimeter. The dilution is determined from a dilution vs. absorbance working curve. The accuracy

of the method is better than $\pm 0.5\%$ proportioning, absolute. Using less dye, an accuracy of $\pm 1\%$ is achieved. This method is applicable to any AFFF concentrate.

3.3

The Water Soluble Dye Approach

A water soluble dye, diphenyl brilliant blue, was obtained from the Dyestuffs and Chemicals Division of Ciba-Geigy Corporation, Greensboro, North Carolina. The Color Index code for this dye is Direct Blue I. A 120-130 ppm solution of the dye was prepared in an experimental, low solvent AFFF concentrate and this solution was diluted from 2% to 10% by volume with natural sea water. The wavelength of minimum percent transmission, i.e., greatest absorbance for the dye, was determined by measuring the percent transmission of a dilution as a function of wavelength. The minimum was found to be at 635 nm. The percent transmission of the prepared dilutions was measured on both a Metrohm Spectrocolorimeter and on the Bausch and Lomb Spectronic Mini 20. The results of those measurements are plotted on the graph in Figure 1. A smooth curve is obtained on either instrument, and the change in per-

cent transmission is sufficient that a difference of 0.5% absolute in proportioning can be determined. Similarly, using 3M LIGHT WATER FC-206 AFFF, curves of % T vs. proportioning were constructed and are shown in Figure 2. The differences in the two curves in Figures 1 and 2 reflect the differences that are typically observed between two instruments. This points up the need to construct a working curve for each AFFF and each instrument. A photograph of AFFF concentrate and selected dilutions in sea water are shown in Figure 3.

In order to reduce the color of the AFFF concentrate and dilutions, the precision of the method with one-third the amount of dye was determined. The curve relating proportioning and percent transmission is shown in Figure 4. A smooth curve is obtained but has less slope than those shown in Figures 1 and 2. The precision of this method is $\pm 1\%$ proportioning absolute. Figure 5 is a photograph of the AFFF concentrate and selected sea water dilutions containing the reduced amount of dye.

3.4

Recommended Procedure

- (a) Adjust the wavelength of the colorimeter to 635 nm.
- (b) Collect a sample of the sea water diluent.

Figure 1. Percent Transmission vs. Proportioning

Experimental low solvent AFFF K76'-312 Containing
120 ppm Dye

Sea Water Dilutions

○ Bausch and Lomb SPECTRONIC MINI 20

□ Metrohm E-1009 Colorimeter

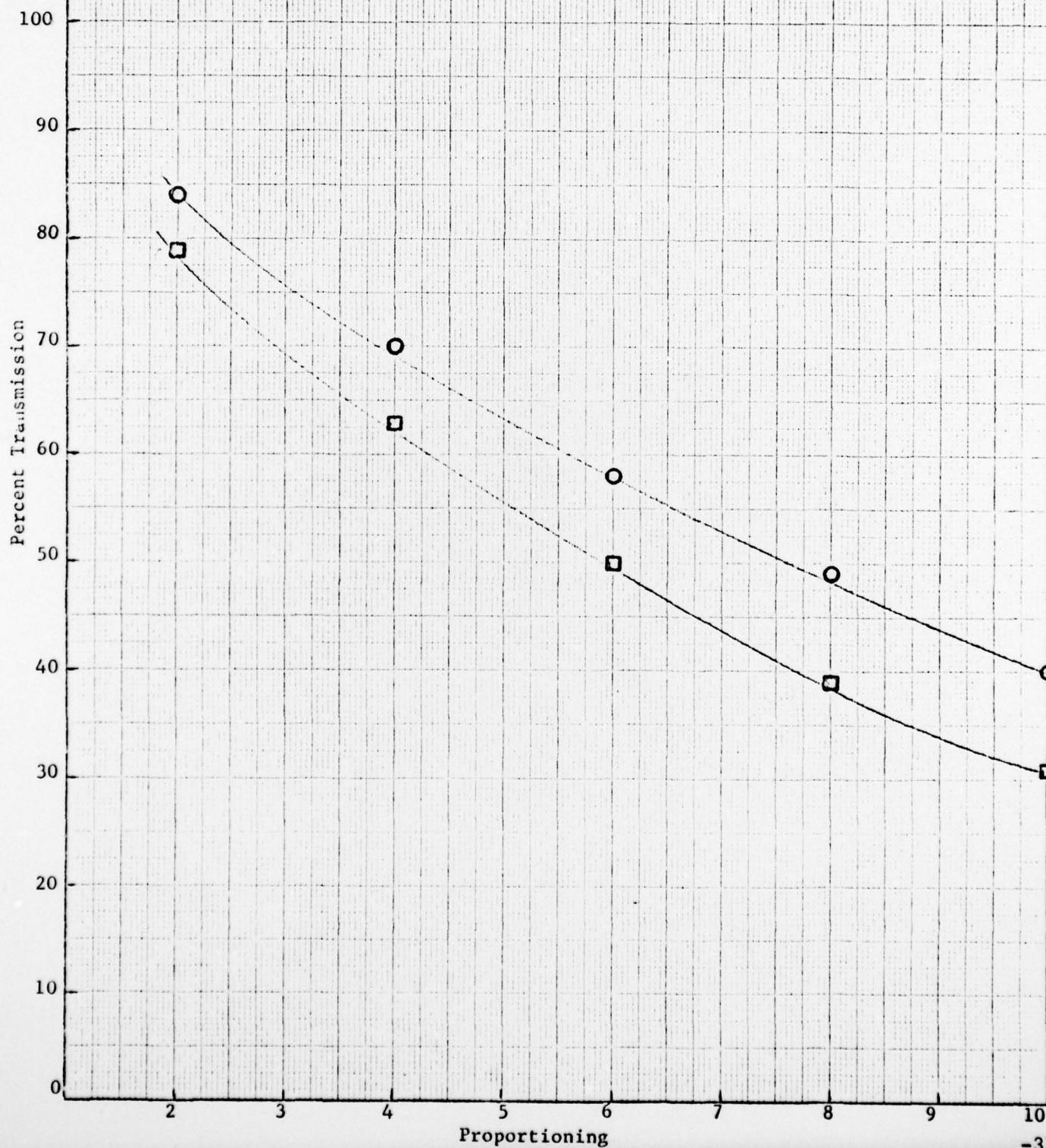
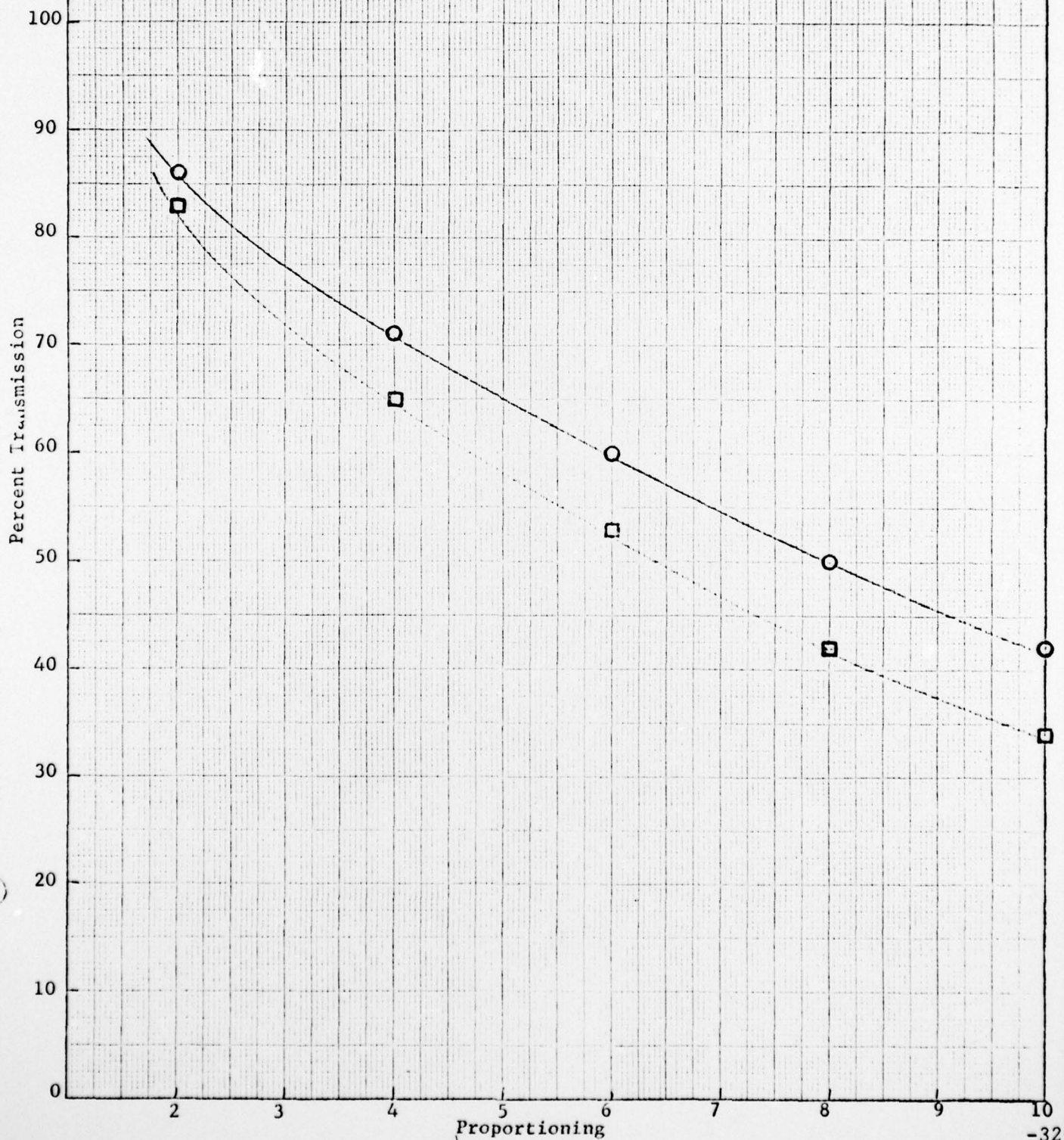


Figure 2. Percent Transmission vs Proportioning
 3M LIGHT WATER⁽⁹⁾ AFFF Containing 120 ppm Dye
 Sea Water Dilutions
 ○ Bausch and Lomb SPECTRONIC MINI 20
 □ Metrohm E 1009 Colorimeter



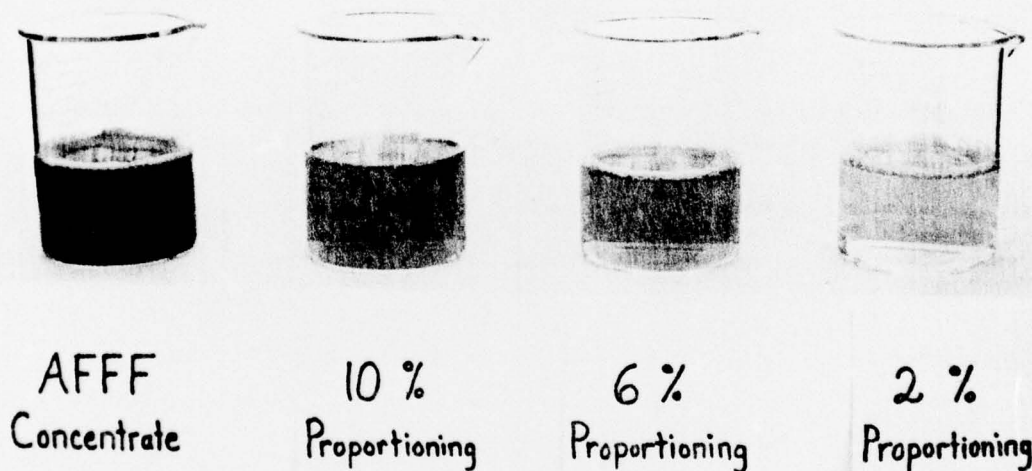
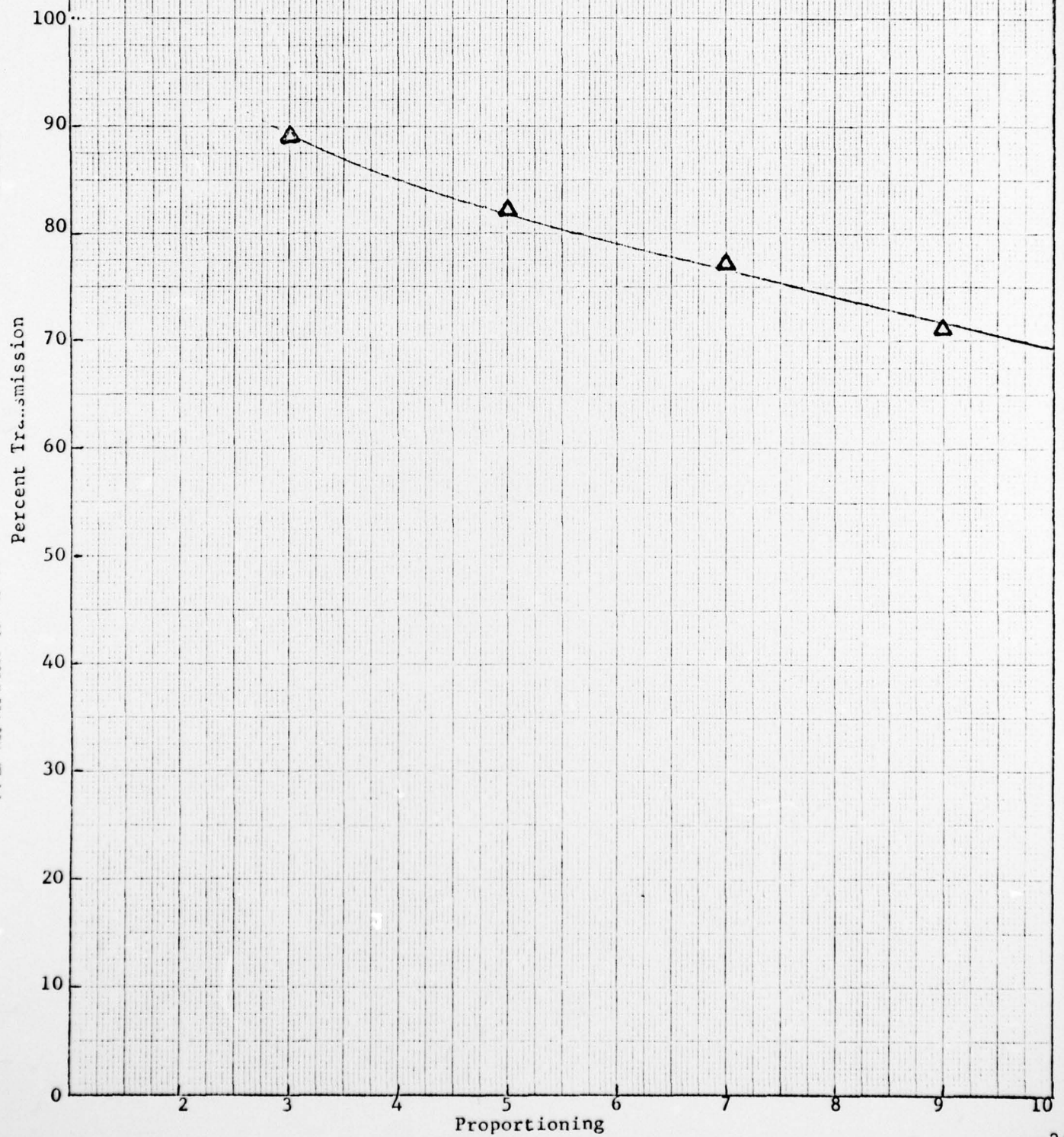


Figure 3. AFFF Concentrate Containing 120 ppm
Dye and Selected Sea Water Dilutions

Figure 4. Percent Transmission vs Proportioning
Experimental low solvent AFFF K76'-312-102
Containing 40 ppm Dye
Sea Water Dilutions



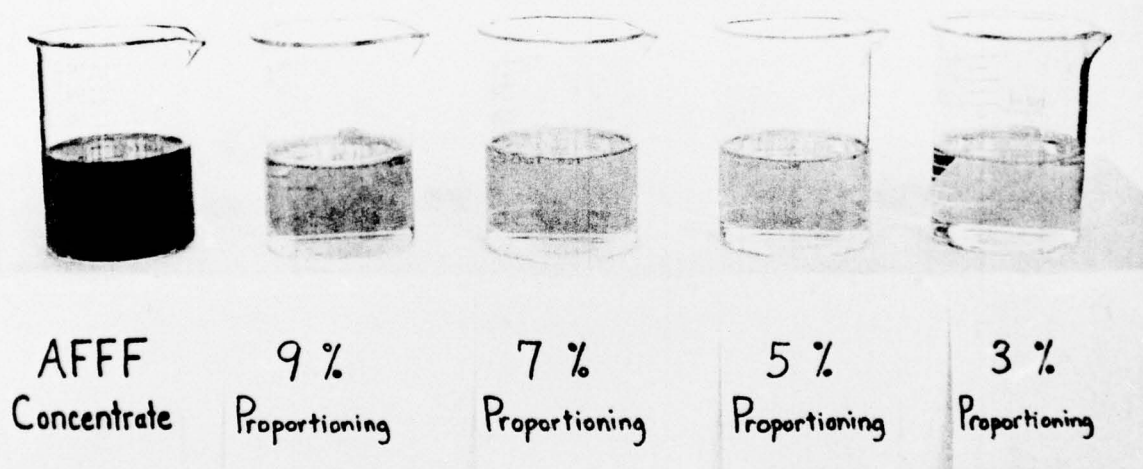


Figure 5. AFFF Concentrate Containing 40 ppm
Dye and Selected Sea Water Dilutions

- (c) Place the sea water diluent in the 1 cm sample cell supplied with the instrument, place the cell in the instrument, and adjust the scale reading to 100% transmission.
- (d) Using the AFFF concentrate in question, containing the dye, construct a working curve of % transmission vs. proportioning using solutions of known dilution and measuring their percent transmission.
- (e) Collect the proportioned solution in question in the usual manner.
- (f) Rinse the cell with the proportioned solution and fill it with the proportioned solution.
- (g) Read the percent transmission and determine the proportioning from the working curve constructed for the AFFF system.

3.5

Experimental

All dilutions were prepared using standard volumetric glassware. The samples used in this study were: (1) A Ciba-Geigy experimental AFFF concentrate containing no added solvent coded K'76-312, and (2) 3M Company FC-206, Lot 11.

Percent transmissions of solutions were measured on a Metrohm Model E 1009 Spectrocolorimeter and/or a Bausch and Lomb Spectronic Mini 20 spectrophotometer. One centimeter path length cuvettes were used throughout.

Synthetic sea water was prepared according to ASTM D-1141-52. Natural sea water was obtained from Long Island Sound.

The water soluble dye used was Ciba-Geigy Diphenyl Brilliant Blue FF Supra 1.

CONCLUSIONS

A series of nine components, consisting of fluorochemical surfactants, hydrocarbon surfactants and solvents, were subjected to 20-day BOD studies as well as COD studies.

These nine components were further reduced to one fluorochemical surfactant, two hydrocarbon surfactants, and two solvent systems based on fire performance using the MIL-F-24385 28 sq.ft. fire test.

A concentration design experiment using the two different hydrocarbon surfactants at two different concentrations and the two solvent systems at two different concentrations was conducted. Aquatic toxicity studies eliminated one of the surfactants and one of the solvent systems.

The concentration experiment showed that the fish toxicity was independent of the composition and the 28 sq.ft. fire performance was equally acceptable at both levels. The major effect of solvent level and hydrocarbon surfactant level is to give a better quality foam with no difference in either extinguishment or 25% burnback resistance. The aquatic toxicity appears to depend on the fluorochemical

surfactant and the hydrocarbon surfactant more than solvent type or concentration.

An alternate method for determining AFFF solution concentration was developed which allows an accuracy of $\pm .5\%$. This method is based upon the measurement of the absorbance of a dye doped solution of AFFF. The method requires the preparation of a calibration curve and is capable of being conducted in the field using an instrument of comparable cost but greater accuracy than the present refractive index method.

It is possible using the levels of components described in this report to formulate AFFF concentrates having acceptable biodegradability ($BOD_{20}/COD > 15$) and aquatic toxicity (LC_{50} 96-hour - 1500 ppm). Further components in aquatic toxicity will require the synthesis of less surface active fluorochemical surfactants which will require some trade-off in fire fighting performance.

BIBLIOGRAPHY

- (1) Technical Report EHL (K) 74-3, Biodegradability and Toxicity of FC-200, Aqueous Film Forming Foam, February 1974.
- (2) Technical Report EHL (K) 75-3, Biodegradability and Toxicity of Ansul K'74-100 Aqueous Film Forming Foam, January 1975.
- (3) Commander NAVFAC Memo, 13 May 1975, Aqueous Film Forming Foam (AFFF), Revised Disposal Guidance.
- (4) Standard Method for the Examination of Waste and Wastewater, APHA, AWWA, WPCF, 12th Edition.
- (5) Standard Marine Bioassay Procedures for Shipboard Chemicals, David W. Taylor, Naval Ship Research and Development Center (DTNSRDC).
- (6) Four-Day Static Aquatic Toxicity on Mummichogs of K'75 268-144, Industrial Bio-Test Laboratories, Inc., January 1976.